

PATENT
 Attorney Docket No. 212691

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

Zaleski et al.

Application No. Unassigned

Filed: August 20, 2001

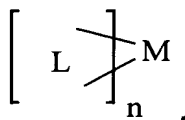
Art Unit: Unassigned

Examiner: Unassigned

For: COMPOUNDS,
 COMPOSITIONS, AND
 METHODS FOR
 PHOTODYNAMIC THERAPY

PENDING CLAIMS AS OF AUGUST 20, 2001

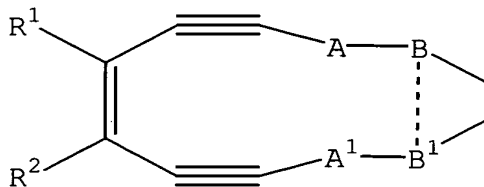
1. A compound of the formula:



wherein M is a metal selected from the group consisting of Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Ga, Tb, Eu, Gd, Dy, Lu, Zr, Nb, Mo, Te, Ru, Rh, Pd, Ag, Sn, Ta, W, Re, Os, Ir, Pt, and Au;

n is an integer from 1-3;

L is a ligand of the formula:



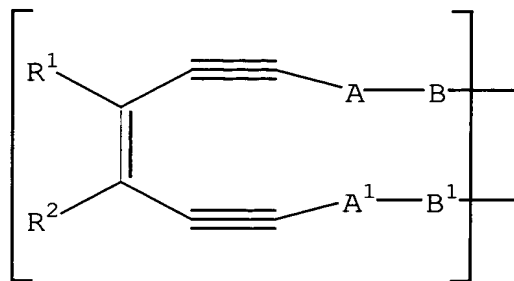
wherein A and A¹ are the same or different and each is independently (CR¹²R¹³)_m, wherein m is an integer from 0 to 6 and wherein R¹² and R¹³ are the same or different and each is hydrogen, halogen, nitro, cyano, azido, an optionally substituted first organic group, or a first solubilizing group;

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B and B¹ are the same or different and each is a substituent comprising a nitrogen-, oxygen-, sulfur-, or phosphorus-containing group capable of complexing with M, wherein the dotted line between B and B¹ represents an optional covalent bond linking B and B¹ together;

R¹ and R² are the same or different and each is independently a hydrogen, a linear or branched alkyl, an aralkyl, an aryl, a halogen, a nitro, or a cyano, or R¹ and R² together with the carbons to which they are bonded comprise an aryl, a heterocycle, or a macrocycle, wherein R¹ and R² is unsubstituted or substituted;

wherein when n is 1 or 2, M is optionally complexed with at least one additional ligand other than a ligand of the formula:



or a dimer, an oligomer, or a polymer of said compound, provided that when m is zero, B and B¹ are not both diphenylphosphine groups.

2. The compound of claim 1, wherein at least one of R¹² and R¹³ is the first organic group optionally substituted with a halogen, nitro, cyano, azido, a second organic group, or a second solubilizing group.

3. The compound of claim 2, wherein the first organic group and the second organic group are the same or different and each is an alkyl or aryl which is optionally substituted with a halogen, nitro, cyano, azido, alkyl, aryl, or a second solubilizing group.

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4. The compound of claim 2, wherein the first solubilizing group and the second solubilizing group are the same or different and each is selected from the group consisting of a hydroxyl, amino or acid addition salt thereof, ammonium salt, carboxylic acid or salt thereof, and sulfonic acid or salt thereof.

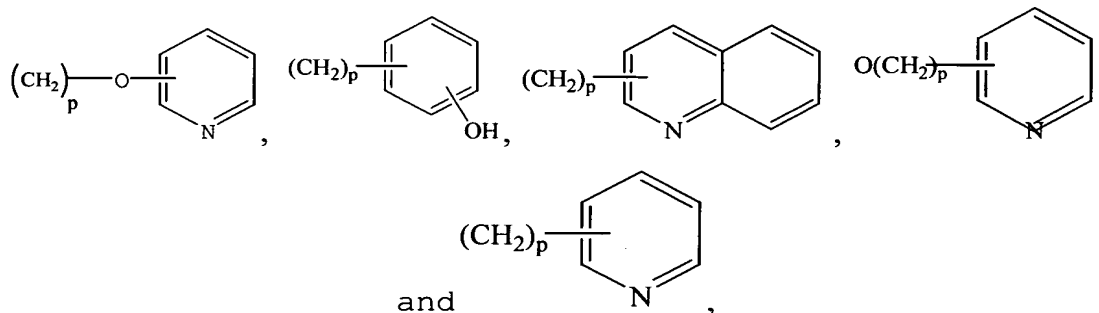
5. The compound of claim 1, wherein M is copper.

6. The compound of claim 1, wherein m is 1.

7. The compound of claim 1, wherein n is 2.

8. The compound of claim 1, wherein at least one of B and B¹ is a nitrogen-containing group capable of complexing with M.

9. The compound of claim 1, wherein at least one of B or B¹ is a nitrogen-containing group selected from the group consisting of substituents characterized by the formulas:



and wherein p is an integer from zero to two.

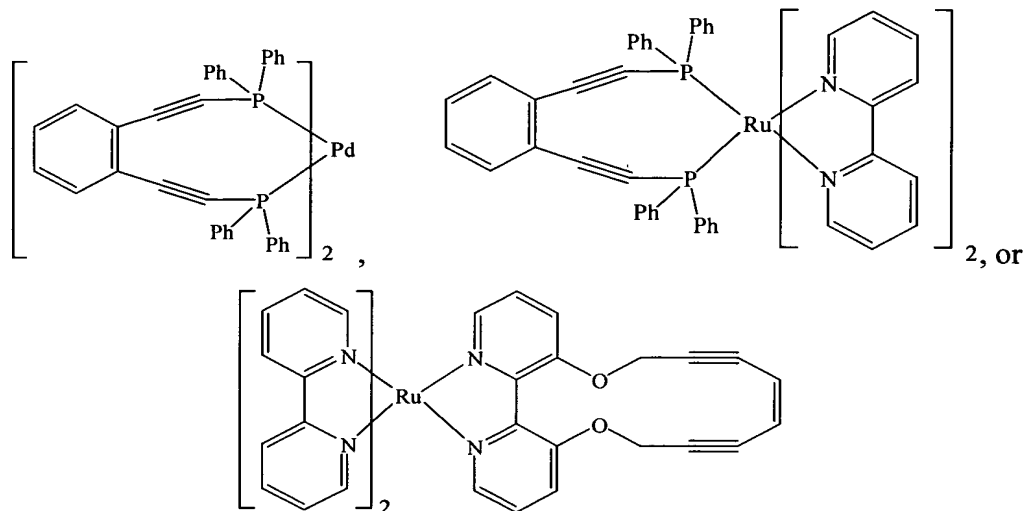
10. The compound of claim 1, wherein B or B¹ is a phosphorus-containing group capable of complexing with M.

11. The compound of claim 10, wherein said phosphorus-containing group is a diarylphosphine.

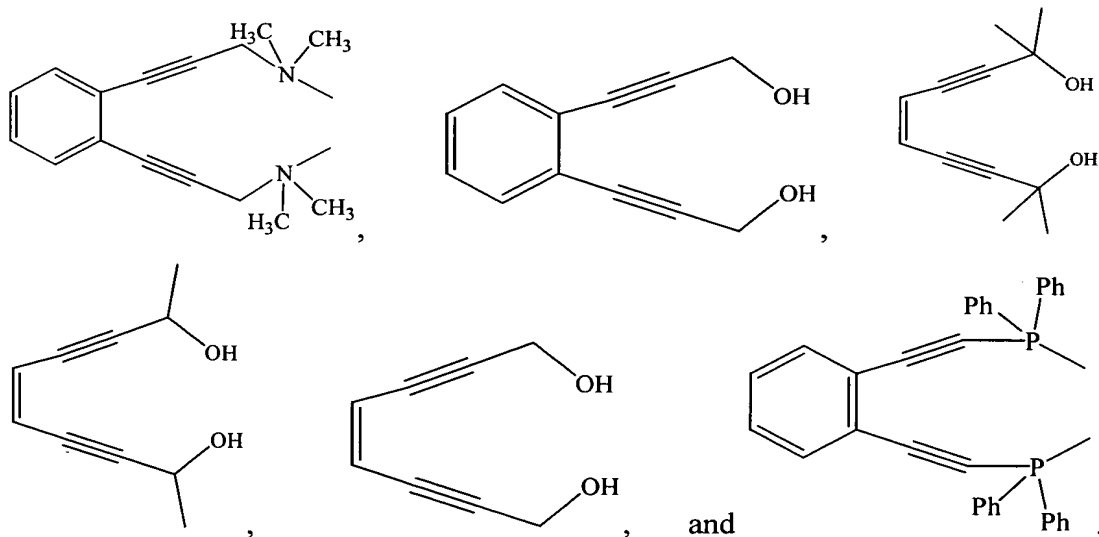
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12. The compound of claim 11, wherein said diarylphosphine is a diphenylphosphine.

13. The compound of claim 1, wherein the compound is of the formula:



14. The compound of claim 1, wherein the compound includes at least one ligand selected from the group consisting of:



15. The compound of claim 1, wherein R^1 and R^2 are the same or different and each is independently selected

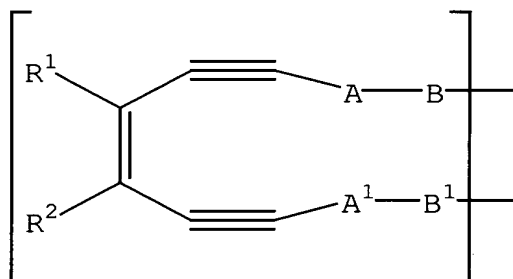
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from the group consisting of hydrogen, an alkyl, an aryl, and an aralkyl, or R^1 and R^2 together with the carbons to which they are bonded comprise a benzene ring.

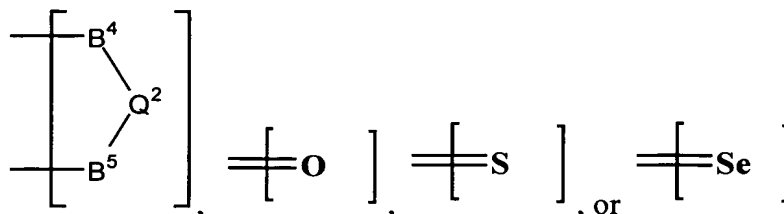
16. The compound of claim 15, wherein at least one of R^1 or R^2 is substituted with a substituent selected from the group consisting of a halogen, a nitro, and a cyano.

17. The compound of claim 15, wherein R^1 and R^2 are hydrogen.

18. The compound of claim 1, wherein n is 1 or 2, and M is complexed with at least one additional ligand other than a ligand of the formula:



19. The compound of claim 18, wherein said at least one additional ligand includes a substituent of the formula:



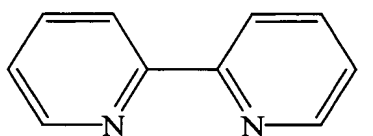
wherein B^4 and B^5 are the same or different and each is nitrogen, oxygen, sulfur, or phosphorus; and Q^2 is an aryl, a heterocycle, a macrocycle, or a C_2 - C_6 alkyl spacer, wherein said aryl, heterocycle, or macrocycle is monocyclic or polycyclic and Q^2 is unsubstituted or substituted.

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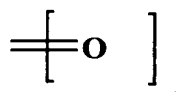
20. The compound of claim 19, wherein Q^2 is a heterocycle.

21. The compound of claim 20, wherein said heterocycle of Q^2 is polycyclic.

22. The compound of claim 21, wherein said polycyclic heterocycle of Q^2 is of the formula:



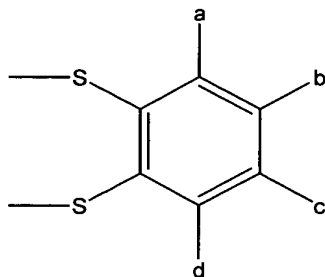
23. The compound of claim 19, wherein said at least one additional ligand includes a ligand of the formula:



24. The compound of claim 19, wherein said Q^2 is bicyclic.

25. The compound of claim 19, wherein Q^2 is an aryl.

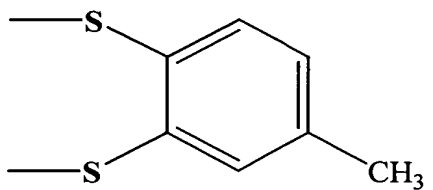
26. The compounds of claim 25, wherein said at least one additional ligand includes a ligand of the formula:



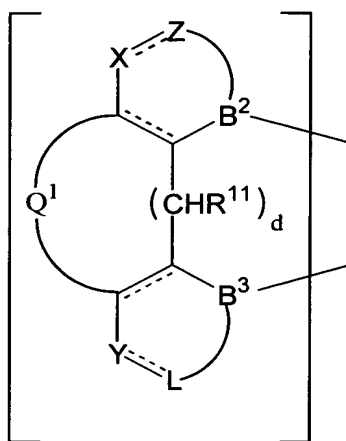
wherein a-d are the same or different and each is selected from the group consisting of hydrogen or alkyl.

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27. The compound of claim 26, wherein said at least one additional ligand includes a ligand of the formula



28. The compound of claim 1, wherein said at least one additional ligand includes a ligand of the formula



wherein R^{11} is a hydrogen or a straight chain or branched alkyl;

d is zero or 1;

B^2 and B^3 are the same or different and are independently selected from nitrogen and sulfur;

Z is a contiguous linker which, together with X , B^2 , and the carbons to which they are bonded, forms a 5- or a 6- membered heterocyclic ring;

L is a contiguous linker which, together with Y , B^3 , and the carbons to which they are bonded, forms a 5- or a 6- membered heterocyclic ring;

the dotted lines represent double bonds optionally present in said 5- or 6- membered heterocyclic ring;

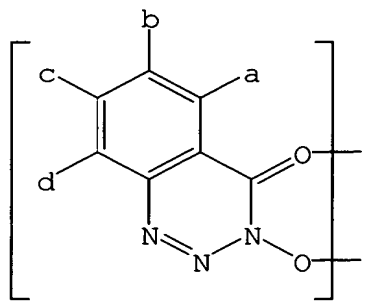
X is N , NR^5 , or CR^5 , wherein R^5 is hydrogen, halogen, or straight chain or branched alkyl;

Y is N , NR^4 , or CR^4 , wherein R^4 is hydrogen, halogen, or straight chain or branched alkyl;

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Q^1 is an organic moiety which includes a diazo group capable of photochemically forming a radical species by the loss of N_2 .

29. The compound of claim 1, wherein said at least one additional ligand includes at least one ligand of the formula



wherein a-d are the same or different and each is hydrogen, halogen, alkyl, OR^{10} , SR^{10} , nitro, and cyano, wherein R^{10} is hydrogen or straight chain or branched alkyl.

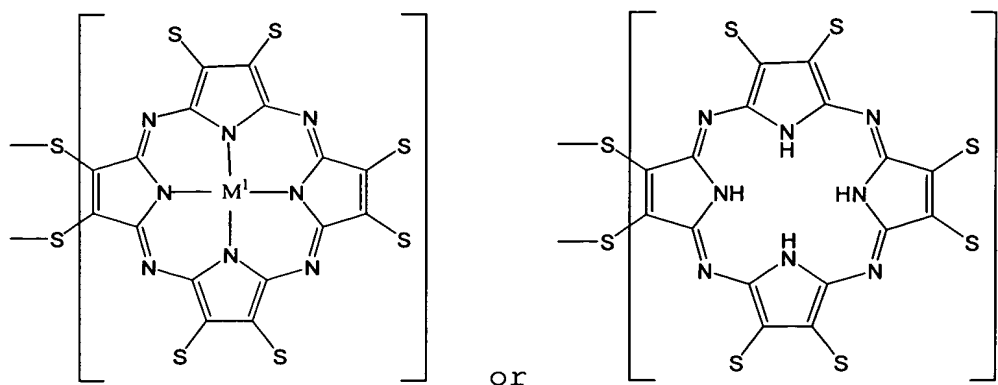
30. The compound of claim 19, wherein said additional ligand is a macrocycle.

31. The compound of claim 30, wherein said macrocycle is selected from the group consisting of porphyrins, porphyrazines, chlorins, phthalocyanines, texaphrins, cyclam, and crown ethers.

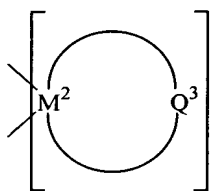
32. The compound of claim 31, wherein said macrocycle is a porphyrin or a porphyrazine.

33. The compound of claim 32, wherein said macrocycle is a porphyrazine of the formula:

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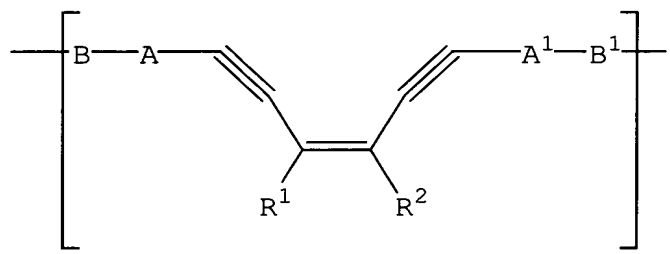


wherein the thiols located within the brackets defining said porphyrazine are uncomplexed or are optionally complexed with at least one additional metal complex of the formula:



wherein M^1 and M^2 are the same or different and each is a metal selected from the group consisting of Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Ga, Tb, Eu, Gd, Dy, Lu, Zr, Nb, Mo, Te, Ru, Rh, Pd, Ag, Sn, Ta, W, Re, Os, Ir, Pt, and Au; and

Q^3 is an enediyne of the formula:



wherein:

A and A^1 are the same or different and each is independently $(CR^{12}R^{13})_m$, wherein m is an integer from 0 to 6 and wherein R^{12} and R^{13} are the same or different and each is hydrogen, halogen, nitro, cyano, azido, an optionally substituted organic group, or a solubilizing group;

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n is an integer from 1-3;

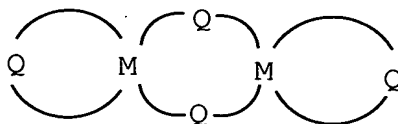
B and B^1 are the same or different and each is a substituent comprising a nitrogen-, oxygen-, sulfur-, or phosphorus-containing group capable of complexing with M , wherein a covalent bond can be optionally present between B and B^1 ;

R^1 and R^2 are the same or different and each is independently a hydrogen, a linear or branched alkyl, an aralkyl, an aryl, a halogen, a nitro, or a cyano, or R^1 and R^2 together with the carbons to which they are bonded comprise an aryl, a heterocycle, or a macrocycle, wherein R^1 and R^2 is unsubstituted or substituted.

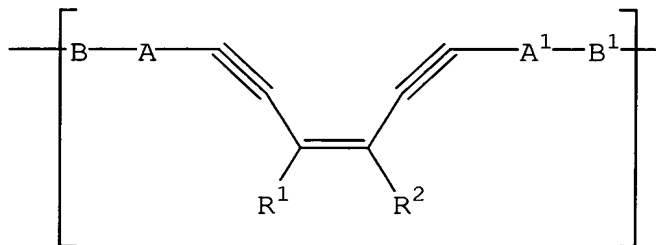
34. The compound of claim 1, wherein said compound is a dimer, an oligomer, or a polymer.

35. The compound of claim 34, wherein said compound is a dimer.

36. The compound of claim 35, wherein said compound is a dimer of the formula:



wherein Q is an enediyne of the formula:



wherein:

A and A^1 are the same or different and each is independently $(CR^{12}R^{13})_m$, wherein m is an integer from 0 to 6 and wherein R^{12} and R^{13} are the same or different and

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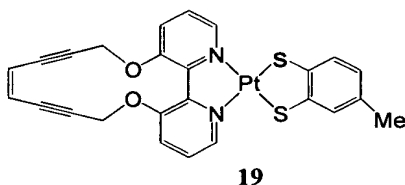
each is hydrogen, halogen, nitro, cyano, azido, an optionally substituted organic group, or a solubilizing group;

n is an integer from 1-3;

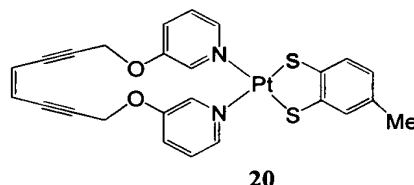
B and B^1 are the same or different and each is a substituent comprising a nitrogen-, oxygen-, sulfur-, or phosphorus-containing group capable of complexing with M , wherein a covalent bond can be optionally present between B and B^1 ;

R^1 and R^2 are the same or different and each is independently a hydrogen, a linear or branched alkyl, an aralkyl, an aryl, a halogen, a nitro, or a cyano, or R^1 and R^2 together with the carbons to which they are bonded comprise an aryl, a heterocycle, or a macrocycle, wherein R^1 and R^2 is unsubstituted or substituted.

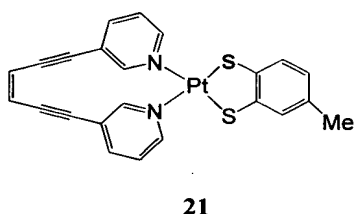
37. The compound of claim 1, wherein the compound is selected from one of the following compounds:



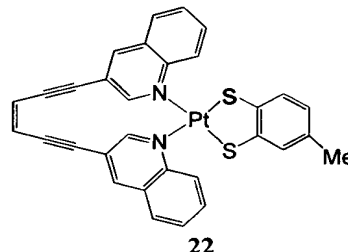
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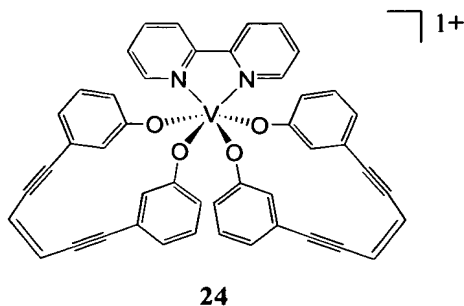
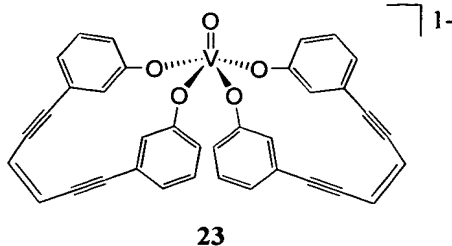


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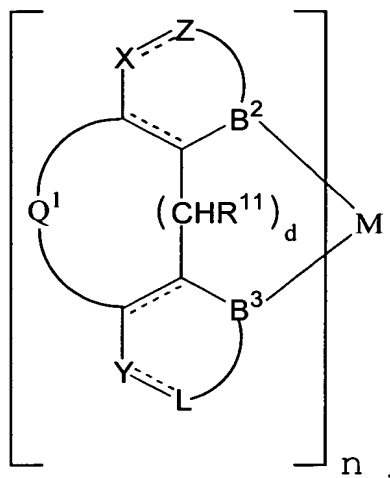
38. The compound of claim 1, wherein said compound is Pd(0)bis[1,2-bis(diphenylphosphinoethynyl)benzene]enediyne.

39. The compound of claim 1, wherein said compound is (1,2-bis(pyridine-3-oxy)oct-4-ene-2,6-diyne)copper(I).

40. The compound of claim 1, wherein said compound is (1,2-bis(pyridine-3-oxy)oct-4-ene-2,6-diyne)copper(II).

41. A compound of the formula:

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wherein M is a metal selected from the group consisting of Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Ga, Tb, Eu, Gd, Dy, Lu, Zr, Nb, Mo, Te, Ru, Rh, Pd, Ag, Sn, Ta, W, Re, Os, Ir, Pt, and Au;

n is an integer from 1 to 3;

R¹¹ is a hydrogen or a straight chain or branched alkyl;

d is zero or 1;

B² and B³ are the same or different and are independently selected from nitrogen and sulfur;

Z is a contiguous linker which, together with X, B², and the carbons to which they are bonded, forms a 5- or a 6- membered heterocyclic ring;

L is a contiguous linker which, together with Y, B³, and the carbons to which they are bonded, forms a 5- or a 6- membered heterocyclic ring;

the dotted lines represent double bonds optionally present in said 5- or 6- membered heterocyclic ring;

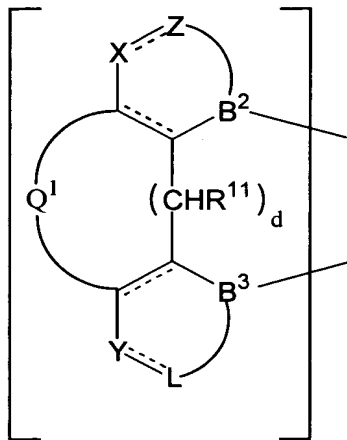
X is N, NR⁵, or CR⁵, wherein R⁵ is hydrogen, halogen, or straight chain or branched alkyl;

Y is N, NR⁴, or CR⁴, wherein R⁴ is hydrogen, halogen, or straight chain or branched alkyl;

Q¹ is an organic moiety which includes a diazo group capable of photochemically forming a radical species by the loss of N₂; and

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wherein when n is 1 or 2, M is optionally complexed with at least one additional ligand other than a ligand of the formula:

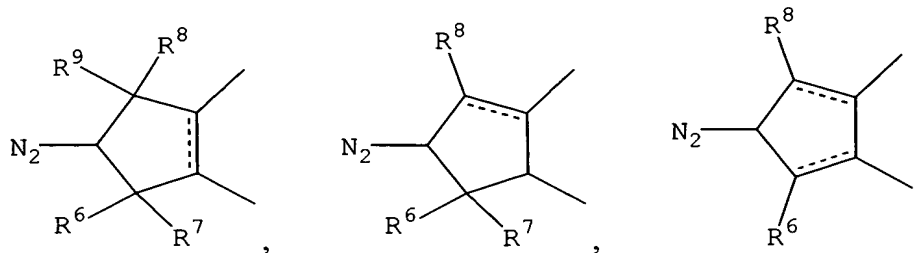


42. The compound of claim 41, wherein said metal is platinum.

43. The compound of claim 41, wherein n is 1.

44. The compound of claim 41, wherein at least one of B^2 and B^3 is nitrogen.

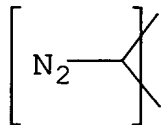
45. The compound of claim 41, wherein said diazo group is a terminal diazo and Q^1 is a substituent of the formula:



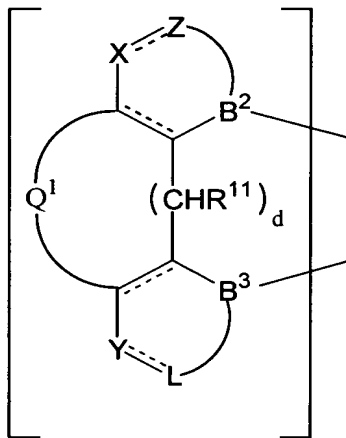
wherein R^6 - R^9 are the same or different and each is independently selected from the group consisting of hydrogen, halogen, cyano, nitro, and a straight chain or branched alkyl; and the dotted lines in the ring defining Q^1 represent double bonds optionally present in said ring.

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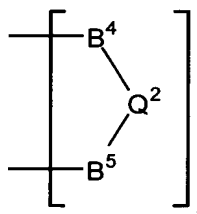
46. The compound of claim 41, wherein said diazo group is a terminal diazo and Q^1 is of the formula:



47. The compound of claim 41, wherein M is complexed with at least one additional ligand other than a ligand of the formula:



48. The compound of claim 47, wherein said additional ligand is a substituent of the formula:

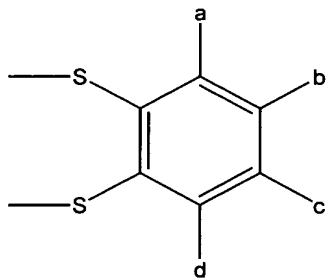


wherein B^4 and B^5 are the same or different and each is nitrogen, oxygen, sulfur, or phosphorus; and Q^2 is an aryl, a heterocycle, a macrocycle, or a C_2 - C_3 alkyl spacer, wherein at least one hydrogen of said alkyl spacer is optionally substituted with an alkyl.

49. The compound of claim 48, wherein Q^2 is an aryl.

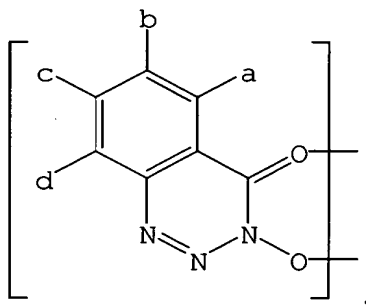
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50. The compounds of claim 49, wherein said additional ligand is of the formula:



wherein a-d are the same or different and each is selected from the group consisting of hydrogen, and straight chain or branched alkyl.

51. The compound of claim 41, wherein said at least one additional ligand includes at least one ligand of the formula



wherein a-d are the same or different and each is hydrogen, halogen, alkyl, OR^{10} , SR^{10} , nitro, and cyano, wherein R^{10} is hydrogen or straight chain or branched alkyl.

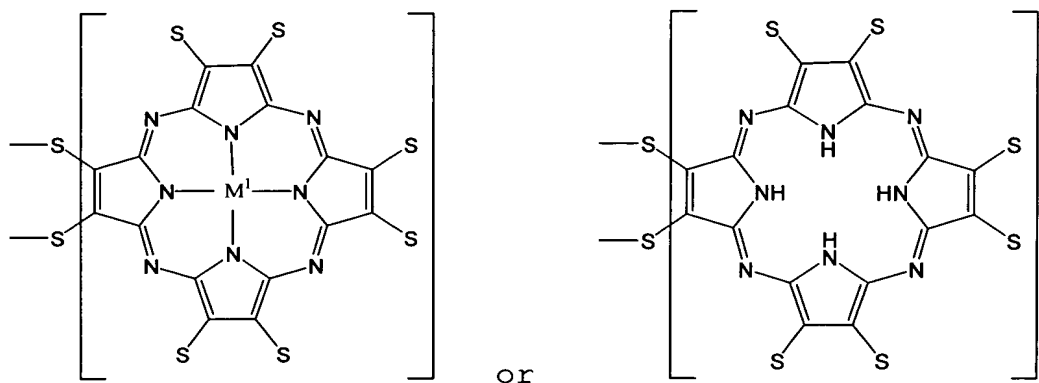
52. The compound of claim 49, wherein said additional ligand is a macrocycle.

53. The compound of claim 52, wherein said macrocycle is selected from the group consisting of porphyrins, porphyrazines, chlorins, phthalocyanines, texaphrins, cyclam, and crown ethers.

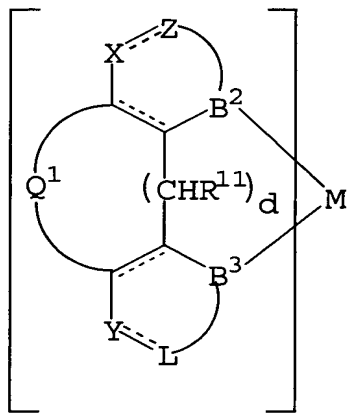
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54. The compound of claim 53, wherein said macrocycle is a porphyrin or a porphyrazine.

55. The compound of claim 53, wherein said macrocycle is a porphyrazine of the formula:



wherein the thiols located within the brackets defining said porphyrazine are uncomplexed or are optionally complexed with at least one additional metal complex of the formula:



wherein M is a metal selected from the group consisting of Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Ga, Tb, Eu, Gd, Dy, Lu, Zr, Nb, Mo, Te, Ru, Rh, Pd, Ag, Sn, Ta, W, Re, Os, Ir, Pt, and Au;

d is zero or 1;

R¹¹ is a hydrogen or a straight chain or branched alkyl;

B² and B³ are the same or different and are independently selected from nitrogen and sulfur;

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Z is a contiguous linker which, together with X, B², and the carbons to which they are bonded, forms a 5- or a 6- membered heterocyclic ring;

L is a contiguous linker which, together with Y, B³, and the carbons to which they are bonded, forms a 5- or a 6- membered heterocyclic ring;

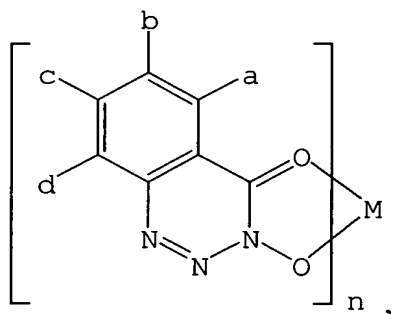
the dotted lines represent double bonds optionally present in said 5- or 6- membered heterocyclic ring;

X is N, NR⁵, or CR⁵, wherein R⁵ is hydrogen, halogen, or straight chain or branched alkyl;

Y is N, NR⁴, or CR⁴, wherein R⁴ is hydrogen, halogen, or straight chain or branched alkyl; and

Q¹ is an organic moiety which includes a diazo group capable of photochemically forming a radical species by the loss of N₂.

56. A compound of the formula:



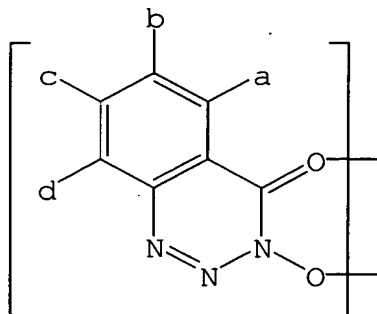
wherein M is a metal selected from the group consisting of Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Ga, Tb, Eu, Gd, Dy, Lu, Zr, Nb, Mo, Te, Ru, Rh, Pd, Ag, Sn, Ta, W, Re, Os, Ir, Pt, and Au;

n is an integer from 1 to 3;

a-d are the same or different and each is hydrogen, halogen, alkyl, OR¹⁰, SR¹⁰, nitro, and cyano, wherein R¹⁰ is hydrogen or straight chain or branched alkyl; and

wherein when n is 1 or 2, M is optionally complexed with at least one additional ligand other than a ligand of the formula:

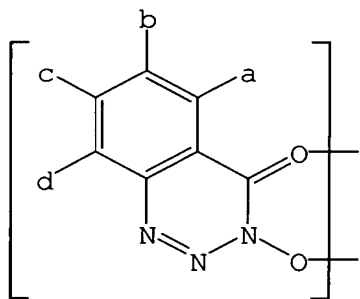
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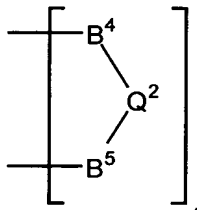
57. The compound of claim 56, wherein M is iron.

58. The compound of claim 56, wherein n is 3.

59. The compound of claim 56, wherein M is complexed with at least one additional ligand other than a ligand of the formula:



60. The compound of claim 59, wherein said additional ligand is a substituent of the formula:

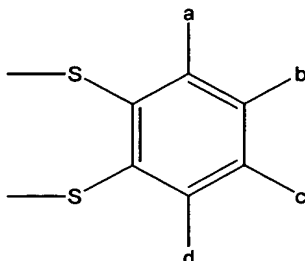


wherein B^4 and B^5 are the same or different and each is nitrogen, oxygen, sulfur, or phosphorus; and Q^2 is an aryl, a heterocycle, a macrocycle, or a C_2 - C_3 alkyl spacer, wherein at least one hydrogen of said alkyl spacer is optionally substituted with an alkyl.

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61. The compound of claim 60, wherein Q^2 is an aryl.

62. The compounds of claim 61, wherein said additional ligand is of the formula:



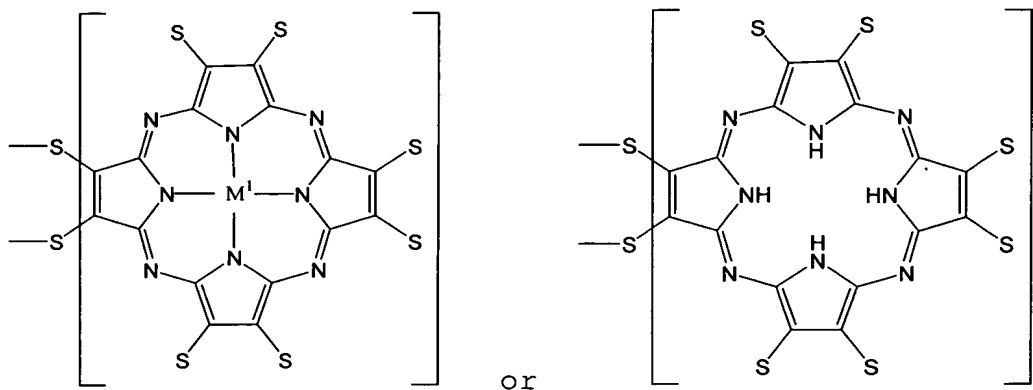
wherein a-d are the same or different and each is selected from the group consisting of hydrogen, and straight chain or branched alkyl.

63. The compound of claim 60, wherein said additional ligand is a macrocycle.

64. The compound of claim 63, wherein said macrocycle is selected from the group consisting of porphyrins, porphyrazines, chlorins, phthalocyanines, texaphrins, cyclam, and crown ethers.

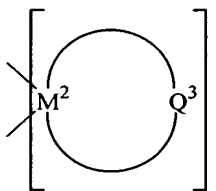
65. The compound of claim 64, wherein said macrocycle is a porphyrin or a porphyrazine.

66. The compound of claim 65, wherein said macrocycle is a porphyrazine of the formula:



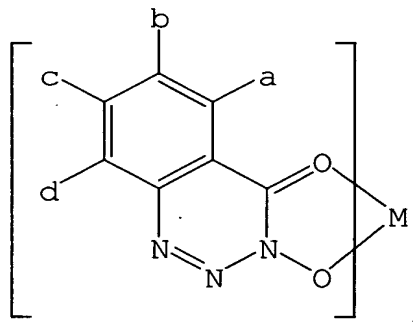
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wherein the thiols located within the brackets defining said porphyrazine are uncomplexed or are optionally complexed with at least one additional metal complex of the formula:



wherein M^1 and M^2 are the same or different and each is a metal selected from the group consisting of Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Ga, Tb, Eu, Gd, Dy, Lu, Zr, Nb, Mo, Te, Ru, Rh, Pd, Ag, Sn, Ta, W, Re, Os, Ir, Pt, and Au; and

Q^3 is of the formula:



wherein M is a metal selected from the group consisting of Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Ga, Tb, Eu, Gd, Dy, Lu, Zr, Nb, Mo, Te, Ru, Rh, Pd, Ag, Sn, Ta, W, Re, Os, Ir, Pt, and Au; and

a-d are the same or different and each is hydrogen, halogen, alkyl, OR^{10} , SR^{10} , nitro, and cyano, wherein R^{10} is hydrogen or straight chain or branched alkyl.

67. A method of treating cancer in a mammal comprising:

contacting said cancer with a therapeutically-effective amount of a compound capable of forming a radical species upon exposure to light by a unimolecular mechanism; and

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irradiating said compound.

68. The method of claim 67, wherein said compound is injected into said mammal so as to contact said cancer.

69. The method of claim 67, wherein said irradiating is at a wavelength of at least about 400 nm.

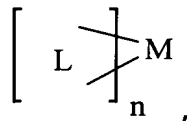
70. The method of claim 69, wherein said irradiating is at a wavelength of at least about 600 nm.

71. The method of claim 70, wherein said irradiating is at a wavelength of at least about 700 nm.

72. The method of claim 67, wherein said cancer is selected from the group consisting of breast metastases, gynecological tumors, cutaneous cancers, Karposi's sarcoma, and papillomatosis.

73. The method of claim 67, wherein said compound is a metalloenediyne.

74. The method of claim 73, wherein said compound is characterized by the formula:

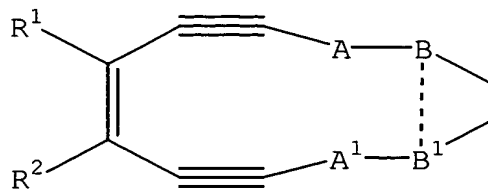


wherein M is a metal selected from the group consisting of Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Ga, Tb, Eu, Gd, Dy, Lu, Zr, Nb, Mo, Te, Ru, Rh, Pd, Ag, Sn, Ta, W, Re, Os, Ir, Pt, and Au;

n is an integer from 1-3;

L is a ligand of the formula:

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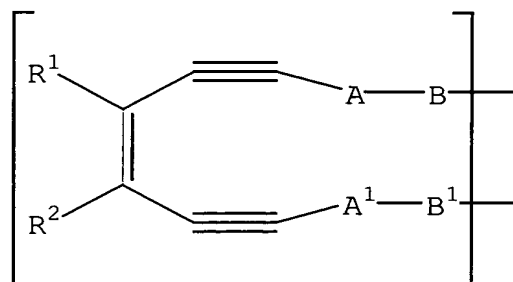


wherein A and A¹ are the same or different and each is independently (CR¹²R¹³)_m, wherein m is an integer from 0 to 6 and wherein R¹² and R¹³ are the same or different and each is hydrogen, halogen, nitro, cyano, azido, an optionally substituted first organic group, or a first solubilizing group;

B and B¹ are the same or different and each is a substituent comprising a nitrogen-, oxygen-, sulfur-, or phosphorus-containing group capable of complexing with M, wherein the dotted line between B and B¹ represents an optional covalent bond linking B and B¹ together;

R¹ and R² are the same or different and each is independently a hydrogen, a linear or branched alkyl, an aralkyl, an aryl, a halogen, a nitro, or a cyano, or R¹ and R² together with the carbons to which they are bonded comprise an aryl, a heterocycle, or a macrocycle, wherein R¹ and R² is unsubstituted or substituted;

wherein when n is 1 or 2, M is optionally complexed with at least one additional ligand other than a ligand of the formula:



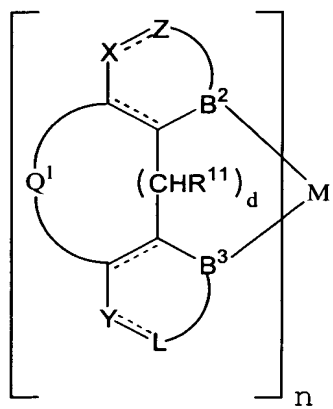
or a dimer, an oligomer, or a polymer of said compound, provided that when m is zero, B and B¹ are not both diphenylphosphine groups.

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75. The method of claim 65, wherein said compound comprises a diazo group that is capable of photochemically forming a radical by the loss of N_2 .

76. The method of claim 75, wherein said compound comprises a macrocycle selected from the group consisting of porphyrins, porphyrazines, chlorins, phthalocyanines, texaphrins, cyclam, and crown ethers.

77. The method of claim 75, wherein said compound is characterized by the formula:



wherein M is a metal selected from the group consisting of Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Ga, Tb, Eu, Gd, Dy, Lu, Zr, Nb, Mo, Te, Ru, Rh, Pd, Ag, Sn, Ta, W, Re, Os, Ir, Pt, and Au;

n is an integer from 1 to 3;

d is zero or 1;

B^2 and B^3 are the same or different and are independently selected from nitrogen and sulfur;

Z is a contiguous linker which, together with X, B^2 , and the carbons to which they are bonded, forms a 5- or a 6- membered heterocyclic ring;

L is a contiguous linker which, together with Y, B^3 , and the carbons to which they are bonded, forms a 5- or a 6- membered heterocyclic ring;

the dotted lines represent double bonds optionally present in said 5- or 6- membered heterocyclic ring;

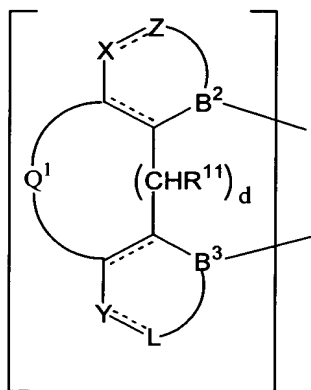
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X is N, NR^5 , or CR^5 , wherein R^5 is hydrogen, halogen, or straight chain or branched alkyl;

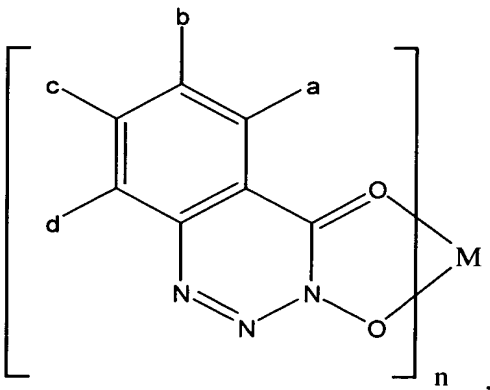
Y is N, NR^4 , or CR^4 , wherein R^4 is hydrogen, halogen, or straight chain or branched alkyl;

Q^1 is an organic moiety which includes a diazo group which is capable of photochemically forming a radical species by the loss of N_2 ; and

wherein when n is 1 or 2, M is optionally complexed with at least one additional ligand other than a ligand of the formula:



78. The method of claim 75, wherein said compound is characterized by the formula:

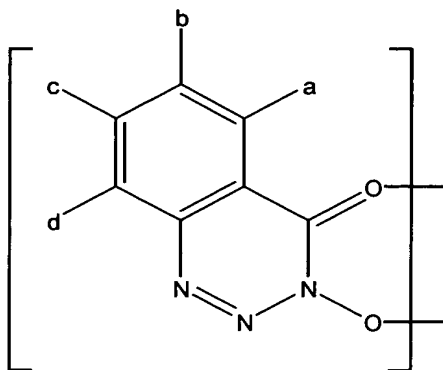


wherein M is a metal selected from the group consisting of Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Ga, Tb, Eu, Gd, Dy, Lu, Zr, Nb, Mo, Te, Ru, Rh, Pd, Ag, Sn, Ta, W, Re, Os, Ir, Pt, and Au;

n is an integer from 1 to 3;

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a-d are the same or different and each is hydrogen, halogen, alkyl, OR^{10} , SR^{10} , nitro, and cyano, wherein R^{10} is hydrogen or straight chain or branched alkyl; and wherein when n is 1 or 2, M is optionally complexed with at least one additional ligand other than a ligand of the formula:



79. A method of treating cancer in a mammal comprising:

contacting said cancer with a therapeutically-effective amount of a compound of claim 1; and
irradiating said compound.

80. The method of claim 79, wherein said compound is injected into said mammal so as to contact said cancer.

81. The method of claim 79, wherein said irradiating is at a wavelength of at least about 400 nm.

82. The method of claim 81, wherein said irradiating is at a wavelength of at least about 600 nm.

83. The method of claim 82, wherein said irradiating is at a wavelength of at least about 700 nm.

84. The method of claim 79, wherein said cancer is selected from the group consisting of breast metastases,

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gynecological tumors, cutaneous cancers, Karposi's sarcoma, and papillomatosis.

85. A method of treating an infection by a microorganism in a mammal comprising:

contacting said microorganism with a therapeutically-effective amount of a compound which forms a radical upon exposure to light by a unimolecular mechanism; and

irradiating said compound.

86. The method of claim 85, wherein said compound is injected into said mammal so as to contact said microorganism.

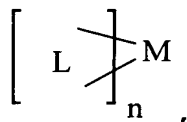
87. The method of claim 85, wherein said irradiating is at a wavelength of at least about 400 nm.

88. The method of claim 87, wherein said irradiating is at a wavelength of at least about 600 nm.

89. The method of claim 87, wherein said irradiating is at a wavelength of at least about 700 nm.

90. The method of claim 85, wherein said compound is a metalloenediyne.

91. The method of claim 90, wherein said compound is characterized by the formula:

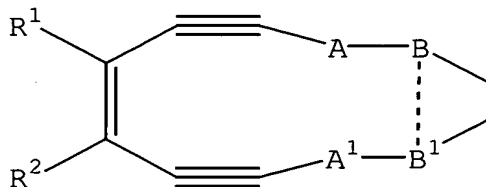


wherein M is a metal selected from the group consisting of Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Ga, Tb, Eu, Gd, Dy, Lu, Zr, Nb, Mo, Te, Ru, Rh, Pd, Ag, Sn, Ta, W, Re, Os, Ir, Pt, and Au;

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n is an integer from 1-3;

L is a ligand of the formula:

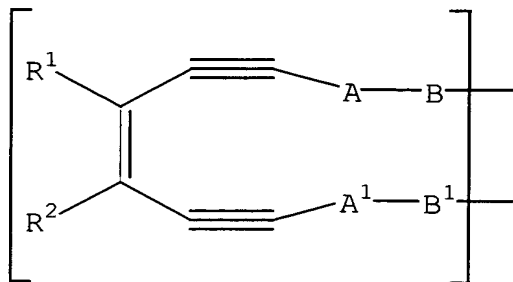


wherein A and A¹ are the same or different and each is independently (CR¹²R¹³)_m, wherein m is an integer from 0 to 6 and wherein R¹² and R¹³ are the same or different and each is hydrogen, halogen, nitro, cyano, azido, an optionally substituted first organic group, or a first solubilizing group;

B and B¹ are the same or different and each is a substituent comprising a nitrogen-, oxygen-, sulfur-, or phosphorus-containing group capable of complexing with M, wherein the dotted line between B and B¹ represents an optional covalent bond linking B and B¹ together;

R¹ and R² are the same or different and each is independently a hydrogen, a linear or branched alkyl, an aralkyl, an aryl, a halogen, a nitro, or a cyano, or R¹ and R² together with the carbons to which they are bonded comprise an aryl, a heterocycle, or a macrocycle, wherein R¹ and R² is unsubstituted or substituted;

wherein when n is 1 or 2, M is optionally complexed with at least one additional ligand other than a ligand of the formula:



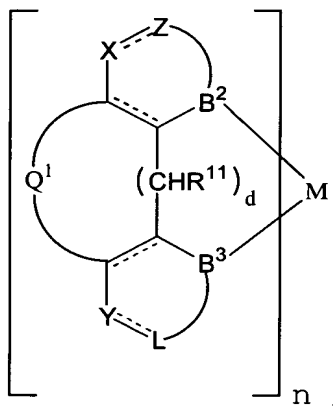
or a dimer, an oligomer, or a polymer of said compound, provided that when m is zero, B and B¹ are not both diphenylphosphine groups.

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92. The method of claim 85, wherein said compound comprises a diazo group, said diazo group being capable of photochemically forming a radical by the loss of N_2 .

93. The method of claim 92, wherein said compound comprises a macrocycle selected from the group consisting of porphyrins, porphyrazines, chlorins, phthalocyanines, texaphrins, cyclam, and crown ethers.

94. The method of claim 92, wherein said compound is characterized by the formula:



wherein M is a metal selected from the group consisting of Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Ga, Tb, Eu, Gd, Dy, Lu, Zr, Nb, Mo, Te, Ru, Rh, Pd, Ag, Sn, Ta, W, Re, Os, Ir, Pt, and Au;

n is an integer from 1 to 3;

d is zero or 1;

B^2 and B^3 are the same or different and are independently selected from nitrogen and sulfur;

Z is a contiguous linker which, together with X, B^2 , and the carbons to which they are bonded, forms a 5- or a 6- membered heterocyclic ring;

L is a contiguous linker which, together with Y, B^3 , and the carbons to which they are bonded, forms a 5- or a 6- membered heterocyclic ring;

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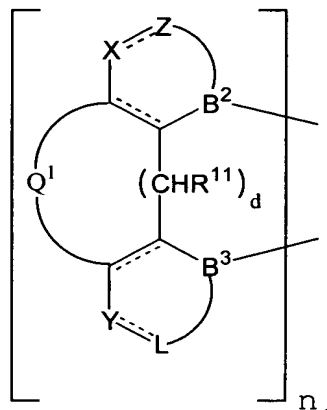
the dotted lines represent double bonds optionally present in said 5- or 6- membered heterocyclic ring;

X is N, NR^5 , or CR^5 , wherein R^5 is hydrogen, halogen, or straight chain or branched alkyl;

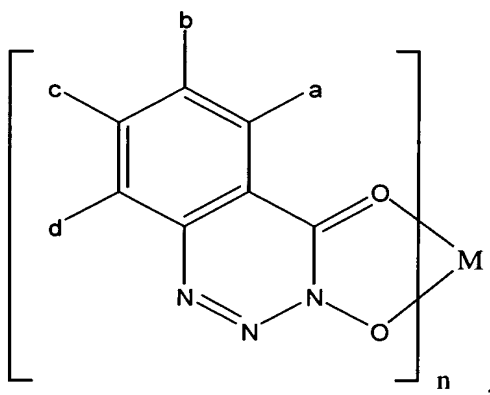
Y is N, NR^4 , or CR^4 , wherein R^4 is hydrogen, halogen, or straight chain or branched alkyl;

Q^1 is an organic moiety which includes a diazo group which is capable of photochemically forming a radical species by the loss of N_2 ; and

wherein when n is 1 or 2, M is optionally complexed with at least one additional ligand other than a ligand of the formula:



95. The method of claim 92, wherein said compound is characterized by the formula:



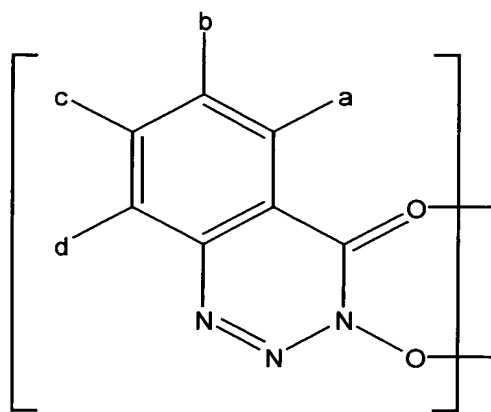
wherein M is a metal selected from the group consisting of Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Ga, Tb, Eu,

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Gd, Dy, Lu, Zr, Nb, Mo, Te, Ru, Rh, Pd, Ag, Sn, Ta, W,
Re, Os, Ir, Pt, and Au;

n is an integer from 1 to 3;

a-d are the same or different and each is hydrogen,
halogen, alkyl, OR^{10} , SR^{10} , nitro, and cyano, wherein R^{10}
is hydrogen or straight chain or branched alkyl; and
wherein when n is 1 or 2, M is optionally complexed with
at least one additional ligand other than a ligand of the
formula:



96. The method of claim 92, wherein said
microorganism is selected from the group consisting of
protozoa, fungi, bacteria, and viruses.

97. A method of treating an infection by a
microorganism in a mammal comprising:

contacting said microorganism with a
therapeutically-effective amount of a compound of claim
1; and

irradiating said compound.

98. The method of claim 97, wherein said compound
is injected into said mammal so as to contact said
microorganism.

99. The method of claim 97, wherein said
irradiating is at a wavelength of at least about 400 nm.

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100. The method of claim 99, wherein said irradiating is at a wavelength of at least about 600 nm.

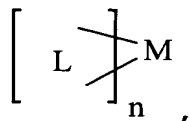
101. The method of claim 100, wherein said irradiating is at a wavelength of at least about 700 nm.

102. The method of claim 97, wherein said microorganism is selected from the group consisting of protozoa, fungi, bacteria, and viruses.

103. A pharmaceutical composition comprising:
a therapeutically effective amount of a compound which forms a radical upon exposure to light by a unimolecular mechanism; and
a pharmaceutically acceptable carrier therefor.

104. The pharmaceutical composition of claim 103, wherein said compound is a metalloenediyne.

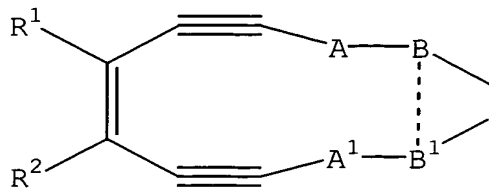
105. The pharmaceutical composition of claim 104, wherein said compound is characterized by the formula:



wherein M is a metal selected from the group consisting of Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Ga, Tb, Eu, Gd, Dy, Lu, Zr, Nb, Mo, Te, Ru, Rh, Pd, Ag, Sn, Ta, W, Re, Os, Ir, Pt, and Au;

n is an integer from 1-3;

L is a ligand of the formula:



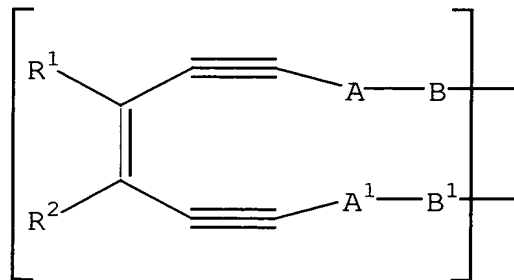
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wherein A and A¹ are the same or different and each is independently (CR¹²R¹³)_m, wherein m is an integer from 0 to 6 and wherein R¹² and R¹³ are the same or different and each is hydrogen, halogen, nitro, cyano, azido, an optionally substituted first organic group, or a first solubilizing group;

B and B¹ are the same or different and each is a substituent comprising a nitrogen-, oxygen-, sulfur-, or phosphorus-containing group capable of complexing with M, wherein the dotted line between B and B¹ represents an optional covalent bond linking B and B¹ together;

R¹ and R² are the same or different and each is independently a hydrogen, a linear or branched alkyl, an aralkyl, an aryl, a halogen, a nitro, or a cyano, or R¹ and R² together with the carbons to which they are bonded comprise an aryl, a heterocycle, or a macrocycle, wherein R¹ and R² is unsubstituted or substituted;

wherein when n is 1 or 2, M is optionally complexed with at least one additional ligand other than a ligand of the formula:



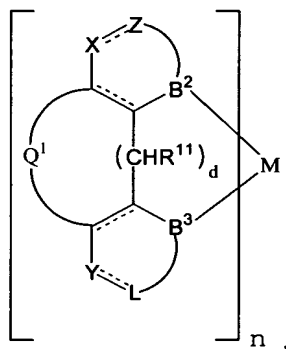
or a dimer, an oligomer, or a polymer of said compound, provided that when m is zero, B and B¹ are not both diphenylphosphine groups.

106. The pharmaceutical composition of claim 103, wherein said compound comprises a diazo group, said diazo group being capable of photochemically forming a radical species by the loss of N₂.

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107. The pharmaceutical composition of claim 105, wherein said compound comprises a macrocycle selected from the group consisting of porphyrins, porphyrazines, chlorins, phthalocyanines, texaphrins, cyclam, and crown ethers.

108. The pharmaceutical composition of claim 103, wherein said compound is characterized by the formula:



wherein M is a metal selected from the group consisting of Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Ga, Tb, Eu, Gd, Dy, Lu, Zr, Nb, Mo, Te, Ru, Rh, Pd, Ag, Sn, Ta, W, Re, Os, Ir, Pt, and Au;

n is an integer from 1 to 3;

d is zero or 1;

B² and B³ are the same or different and are independently selected from nitrogen and sulfur;

Z is a contiguous linker which, together with X, B², and the carbons to which they are bonded, forms a 5- or a 6- membered heterocyclic ring;

L is a contiguous linker which, together with Y, B³, and the carbons to which they are bonded, forms a 5- or a 6- membered heterocyclic ring;

the dotted lines represent double bonds optionally present in said 5- or 6- membered heterocyclic ring;

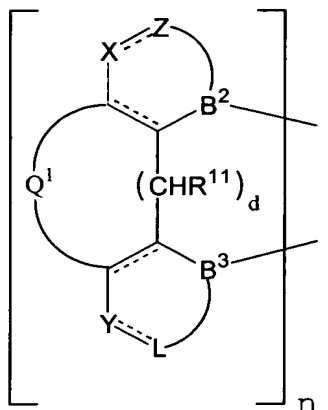
X is N, NR⁵, or CR⁵, wherein R⁵ is hydrogen, halogen, or straight chain or branched alkyl;

Y is N, NR⁴, or CR⁴, wherein R⁴ is hydrogen, halogen, or straight chain or branched alkyl;

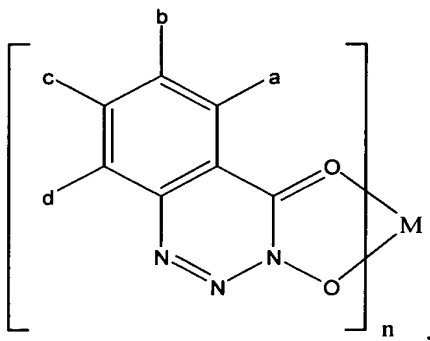
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Q^1 is an organic moiety which includes a diazo group which is capable of photochemically forming a radical by the loss of N_2 ; and

wherein when n is 1 or 2, M is optionally complexed with at least one additional ligand other than a ligand of the formula:



109. The pharmaceutical composition of claim 105, wherein said compound is characterized by the formula:



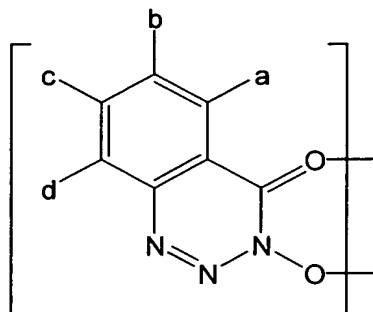
wherein M is a metal selected from the group consisting of Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Ga, Tb, Eu, Gd, Dy, Lu, Zr, Nb, Mo, Te, Ru, Rh, Pd, Ag, Sn, Ta, W, Re, Os, Ir, Pt, and Au;

n is an integer from 1 to 3;

$a-d$ are the same or different and each is hydrogen, halogen, alkyl, OR^{10} , SR^{10} , nitro, and cyano, wherein R^{10} is hydrogen or straight chain or branched alkyl; and wherein when n is 1 or 2, M is optionally complexed with

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at least one additional ligand other than a ligand of the formula:



110. The pharmaceutical composition of claim 103, wherein said composition is used to treat cancer in a mammal.

111. The pharmaceutical composition of claim 103, wherein said composition is used to treat an infection by a microorganism in a mammal, wherein said microorganism is selected from the group consisting of protozoa, fungi, bacteria, and viruses.

112. The pharmaceutical composition of claim 103, wherein said composition is suitable for injection to a desired site in a mammal.

113. A pharmaceutical composition comprising:
a therapeutically effective amount of a compound of claim 1; and
a pharmaceutically acceptable carrier therefor.

114. The pharmaceutical composition of claim 113, wherein said composition is used to treat cancer in a mammal.

115. The pharmaceutical composition of claim 113, wherein said composition is used to treat an infection by a microorganism in a mammal, wherein said microorganism

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is selected from the group consisting of protozoa, fungi, bacteria, and viruses.

116. The pharmaceutical composition of claim 113, wherein said composition is suitable for injection to a desired site in a mammal.